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TEMPERATURE-VISCOSITY RELATIONS IN THE TERNARY SYSTEM CaO-Al_2O_3-SiO_2

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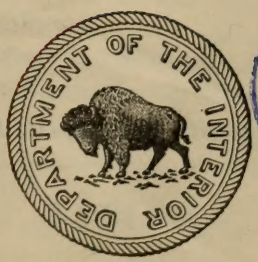
BY

ALEXANDER L. FEILD AND P. H. ROYSTER



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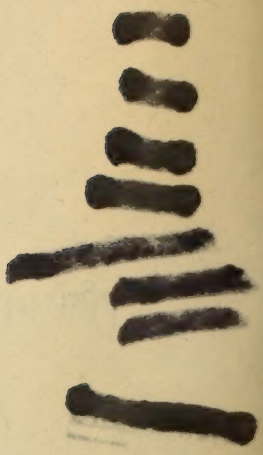

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TEMPERATURE-VISCOSITY RELATIONS IN THE TERNARY SYSTEM CaO-Al_2O_3-SiO_2.

By Alexander L. Feild and P. H. Royster.

INTRODUCTION.

In the course of the investigations of blast-furnace slags being conducted by the Bureau of Mines with a view to increasing efficiency and economy in the smelting of iron ores, a number of determinations of the temperature-viscosity relations of silicates at high temperatures were made. The methods of measurement, apparatus, and laboratory procedure used in these experiments have been described in Technical Paper 157, "A New Method for Measuring the Viscosity of Blast-Furnace Slags at High Temperatures." Temperature-viscosity tables prepared from the data have beeen published in Technical Paper 187, "Slag Viscosity Tables for Blast-Furnace Work."

This report presents the results of observations on the temperature-viscosity relations of silicates representing a part of the ternary system CaO-Al_2O_3-SiO_2, and is presented by the bureau as a contribution to the present knowledge of the properties of these silicates at high temperatures. The results presented have a direct relation to many problems outside of the field of iron metallurgy.

SCOPE OF REPORT.

In many industrial processes it is desired to know something about the more general physical and chemical properties of silicates. In the manufacture of refractories, Portland cement, glass, and porcelain, and in pyrometallurgical work, the behavior of silicate compounds at temperatures beyond the range of common experience is important. This field of research has not been investigated as carefully as its scientific and industrial importance seems to warrant. In the course of investigating the composition and properties of blast-

furnace slags the writers have had occasion to determine the temperature-viscosity relations for a part of the ternary system CaO-Al_2O_3-SiO_2[a]. As many of the results seem to bear directly on the question of the structure of these silicates, a brief description of them is given in this report. The investigation was confined to that range of composition encountered in iron blast-furnace slags, and a complete study of the system has not been made. However, some important conclusions have been drawn from the experiments.

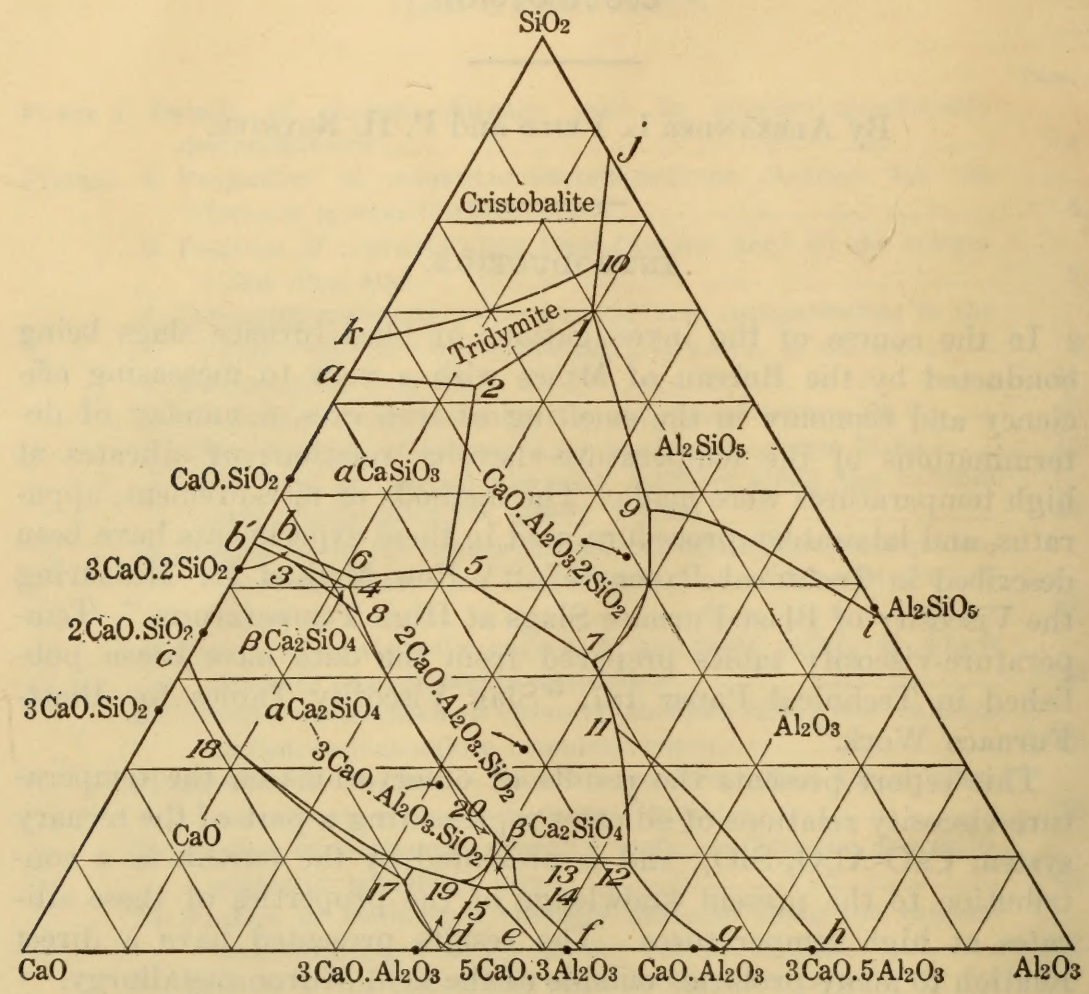


FIGURE 1.—Projection of concentration-temperature diagram for the ternary system CaO-Al_2O_3-SiO_2, showing compositions whose primary phases determined the position of boundary curves and quintuple points. After Rankin and Wright.

The stability relations of the system investigated have been published by Rankin and Wright.[b] A diagram taken from their paper, which shows the stability fields of the 14 compounds observed by them, is shown in figure 1. In parts of the fields of calcium metasilicate ($CaSiO_3$) and gehlenite ($Ca_2Al_2SiO_7$) the writers made viscosity measurements with some completeness. This area is shown in fig-

[a] Feild, A. L., and Royster, P. H., Slag viscosity tables for blast-furnace work: Tech. Paper 187, Bureau of Mines, 1918, 38 pp.

[b] Rankin, G. A., and Wright, F. E., Ternary system CaO-Al_2O_3-SiO_2: Am. Jour. Sci., ser. 4, vol. 39, 1915, pp. 1–79.

ure 2.[a] The reason for selecting this region for investigation is indicated by the positions of the 25 points given in the figure; these correspond to compositions of representative slags from 28 (3 lie outside of the area represented by the figure) blast-furnace plants, which cover 44 per cent of the total pig iron production of the United States.

SILICATES IN THE LIQUID STATE.

One of the most important of the unsolved problems in the chemistry of silicates is that of their stability in the liquid state.

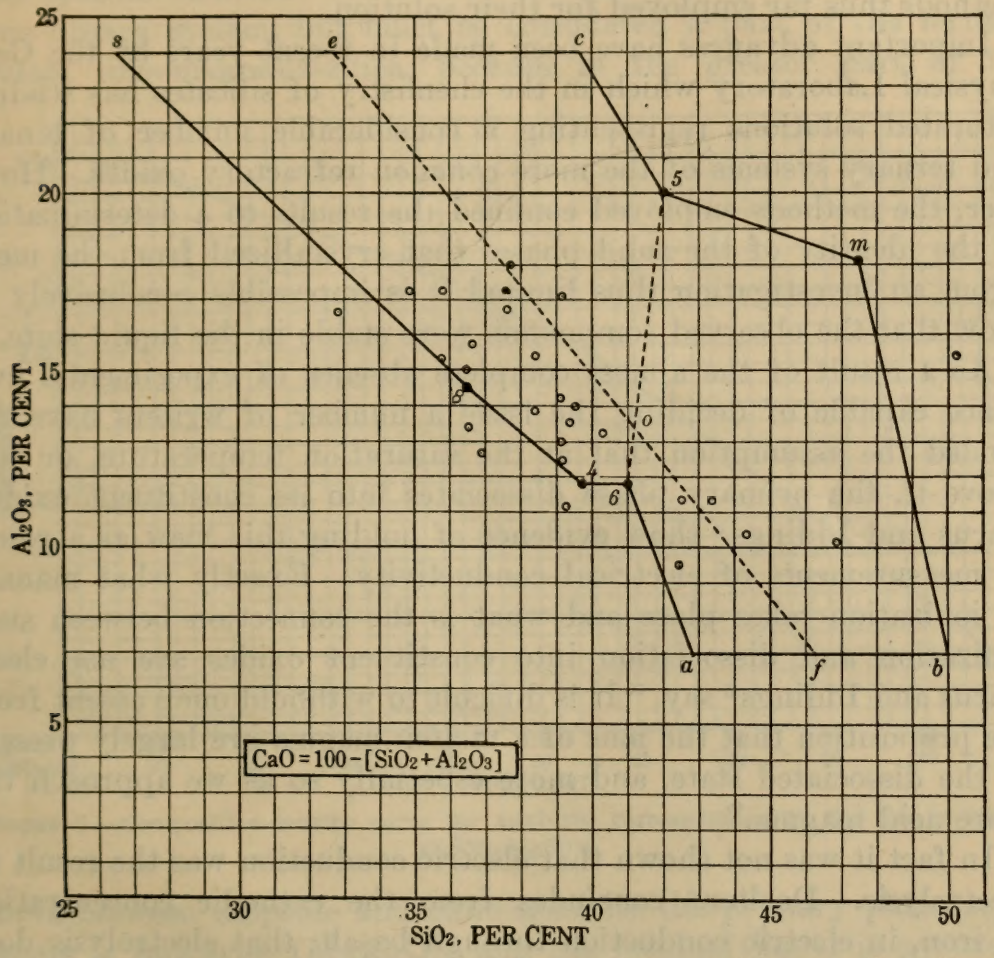


FIGURE 2.—Position of representative blast-furnace slags on the composition diagram. The area *a b m 5 6* represents part of the stability field of calcium metasilicate; the area *6 5 c s 4*, part of the stability field of gehlenite.

Progress toward the solution of this problem has been small because of the difficulties that attend experiments at temperatures at which silicates become fluid and the comparatively short time since these temperatures could be measured. On the other hand, considerable

[a] In a ternary system any two components may be chosen as independent variables. The authors have found it convenient to represent these two variables by the usual rectangular coordinates. As the composition of a ternary system possesses only two degrees of freedom, if oblique coordinates are used, there is danger of mistaking the number of variables for three.

progress has been made in the study of the silicate compounds in the solid state because of the directness and simplicity of methods of optical examination. As a result the present state of knowledge regarding the silicates is in an analogous condition. The methods of physical chemistry have proved more successful with liquids and liquid solutions than with solids; so that our knowledge of the molecular state of aggregation of most chemical compounds can be said almost to be confined to the chemistry of solute and of liquid solvents. That the silicates are an exception to this rule is a result not of any peculiarity of the problems dealt with, but rather of the methods thus far employed for their solution.

Important advances have been made in recent years by the Geophysical Laboratory which in the chemistry of silicates has studied saturated solutions representing a considerable number of binary and ternary systems of the more common refractory oxides. However, the methods employed confined the results to a determination of the identity of the solid phases that crystallized from the melt. From an investigation thus limited it is impossible conclusively to show that the observed compounds were stable in the liquid state.

As a result of the almost complete absence of experimental evidence capable of deciding the issue a number of writers have defended the assumption that at the saturation temperature, or just above it, the primary phase dissociates into its constituent oxides. Barus and Iddings[a] show evidence of holding this view as a result of measurements of electrical conductivity. Exactly what manner of ionization takes place and what is the connection between such ionization and dissociation into constituent oxides are not clear. Barus and Iddings[b] say, "It is difficult to withhold one's assent from the proposition that the ions of a molten magma are largely present in the dissociated state, and more especially so as we approach the more acid magma."

In fact it was not shown that electric conduction was the result of electrolysis. Doelter[c] concludes from the cathodic concentration of iron, in electric conduction through basalt, that electrolysis does exist. Lowinson-Lessing and Vogt,[d] on the other hand, maintain the existence of undecomposed silicate molecules in the liquid state.

The most direct evidence in support of the contention that certain compounds are subject to purely thermal dissociation has been given by Sosman,[e] and is briefly this. For the so-called binary system

[a] Barus, Carl, and Iddings, J. P., Note on the change of electric conductivity observed in rock magmas of different composition on passing from liquid to solid: Am. Jour. Sci., ser. 3, vol. 44, 1892, pp. 242–249.

[b] Barus, Carl, and Iddings, J. P., work cited, p. 249.

[c] Doelter, Cornelio, Handbuch der Mineralchemie, vol. 1, 1912, p. 712.

[d] See Doelter, Cornelio, work cited, p. 712.

[e] Sosman, R. B., The common refractory oxides: Jour. Ind. and Eng. Chem., vol. 8, 1916, pp. 985–990; Trans. Faraday Soc., vol. 12, 1916, pp. 170–179.

$CaSiO_3$ (pseudowollastonite) and $MgSiO_3$ (clino-enstatite) the specific volume for the crystalline state exhibits a maximum of condensation at the molecular proportions 1:1, corresponding to the double silicate $CaMgSi_2O_6$ (diopside). In the glassy state no such singular point was noted. The experimental data used by Sosman, taken presumably from Larsen,[a] are shown in figure 3. Unfortunately, as will be seen, these data do not permit a conclusive decision as to the continuity of the slope of the composition-density curve shown in the figure.[b] Still more unfortunate was the selection of this system. Bowen[c] has shown that these compositions are not a true binary system, but must be considered a part of the ternary system lime-magnesia-silica, because in the greater part of the

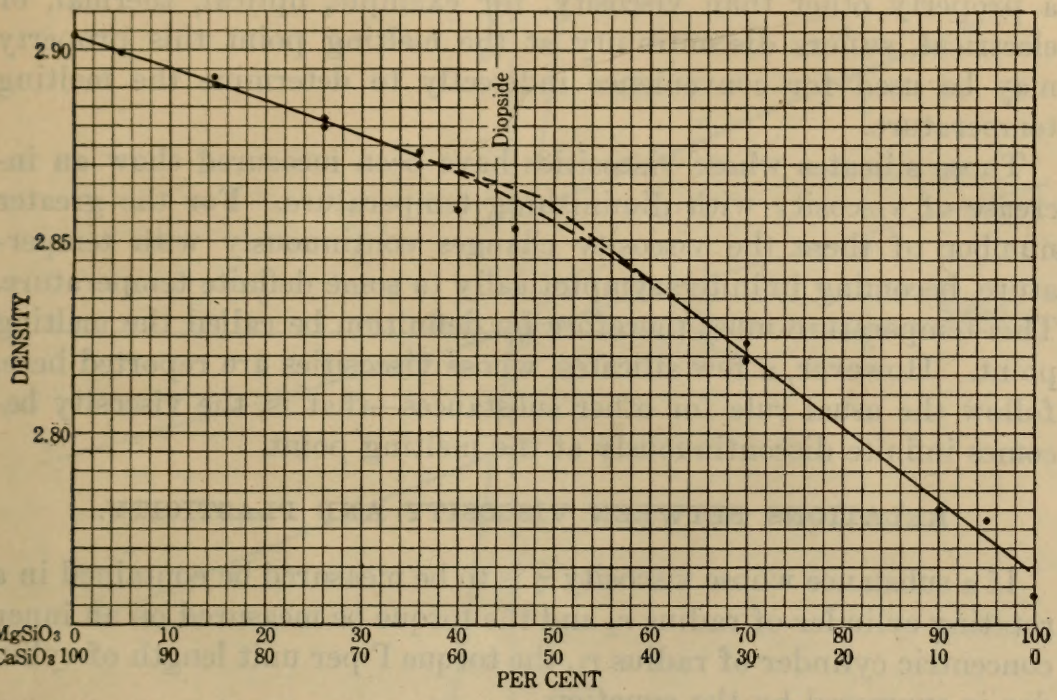


FIGURE 3.—Composition-density curve for mixtures corresponding to the binary system $CaSiO_3$-$MgSiO_3$.

curve between diopside and clino-enstatite the primary phase separating is forsterite (Mg_2SiO_4) and the residual liquid is pyroxene, a member of an isomorphic series yielding, on cooling, a solid solution. The calcic end of the curve has not been investigated as a part of its ternary system.

That the conclusions that have been drawn as to the existence of liquid silicate compounds were based upon incomplete evidence

[a] Larsen, E. S., The relation between the refractive index and the density of some crystallized silicates and their glasses: Am. Jour. Sci., ser. 4, vol. 28, 1909, pp. 263–274.

[b] The points at 40 and 46 per cent magnesium metasilicate must be left out of account in drawing any reasonably smooth curve. The two dotted parts of the curve shown in figure 3 are equally probable. If specific volume be used as ordinate, no improvement is observed.

[c] Bowen, N. L., The ternary system diopside-forsterite-silica: Am. Jour. Sci., ser. 4, vol. 38, 1914, p. 218.

of this nature shows the need of direct experiments on silicates in the liquid state.

THE VISCOSITY OF SILICATES.

The changes accompanying the transition from solid to liquid of silicates are shared by few substances. As a general rule, the physical properties of a body are subject to discontinuity at its melting point, but this rule does not hold for silicates. The definition of a solid given by Maxwell[a] is that its viscosity be infinite. As the definition of a solid thus depends on the physical property of viscosity it is evident that the final determination of the melting point of a body will involve alone a determination of its viscosity. Where a property other than viscosity, for example, optical, thermal, or electrical, suffers discontinuity at the melting point this property may be used for convenience indirectly to determine the melting temperature.

Those silicates whose viscosities have been measured show an increase of viscosity with diminishing temperature. For the greater number of them the viscosity changes continuously with temperature, becoming infinite asymptotically to some definite temperature. This temperature must therefore by definition be called the melting point. However, a few silicates, whose viscosities are reported here, follow the usual rule for other substances—that is, the viscosity becomes infinite discontinuously at the melting point.

RELATIONS BETWEEN VISCOSITY AND PLASTICITY.

If a substance whose viscosity η is to be measured be contained in a rotating cylinder of radius r_2 and the torque be measured on an inner concentric cylinder of radius r_1, the torque Γ per unit length of cylinder is expressed by the equation

$$\Gamma = C\omega$$

where ω is the angular velocity of the outer cylinder and where

$$C = 4\pi\eta \frac{r_1 r_2}{r_2^2 - r_1^2}$$

It must be assumed in deriving this expression that the viscosity is not a function of the transverse velocity gradient. For any actual substance a departure from this ideal condition is possible in two ways: (1) The torque may not vary linearly with the speed of rotation, or (2) the torque may not vanish with the speed. Although it is probable that in no instance is there a strictly linear relation, the deviation from linearity in the measurements that are

[a] Maxwell, J. C., Scientific Papers, vol. 2 (Cambridge, 1890), p. 620.

being described was less than the known experimental error. For nearly all of the silicate mixtures examined a residual torque was observed, when the outer cylinder was brought to rest, that was greater than could be attributed to a possible experimental error. That a substance can possess rigidity under an applied shear below a certain limiting value and exhibit fluidity for shears greater than this limiting value has been long recognized for those bodies variously termed malleable, ductile, and plastic "solids." Their behavior differs from that of the silicate mixtures only in that the order of magnitude of the rigidity modulus, the viscosity, and the limiting shear is much greater.

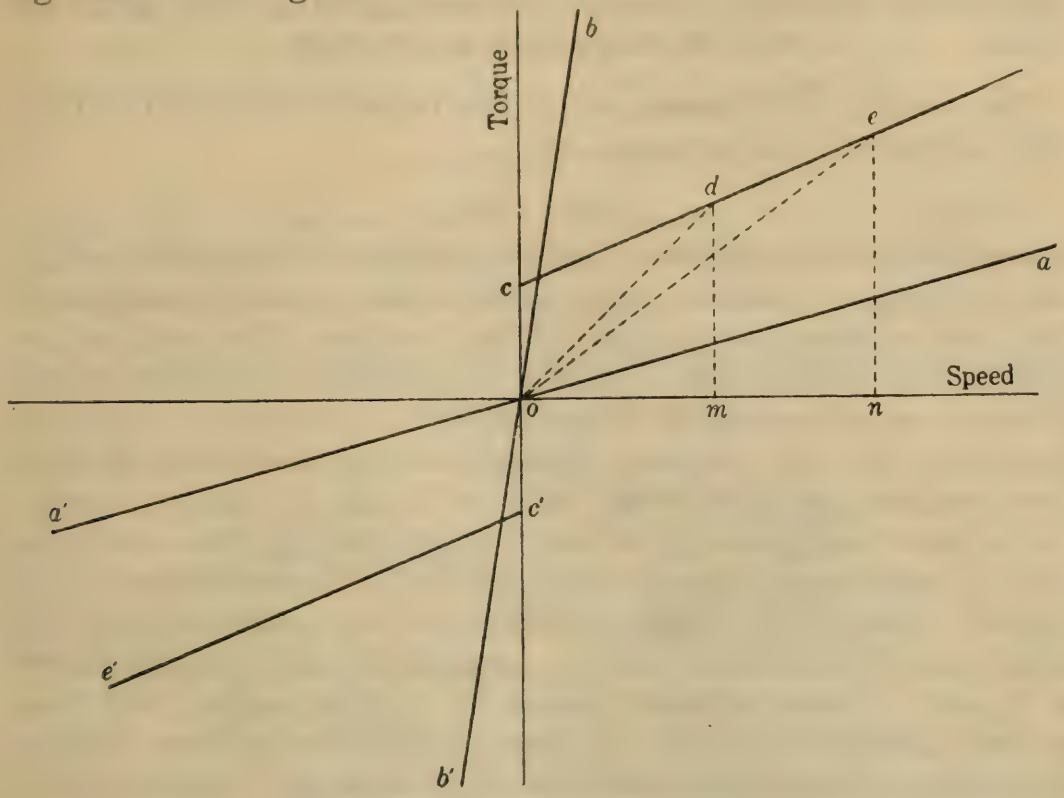


FIGURE 4.—Torque-speed diagram.

These relations may be better understood perhaps by reference to the torque-speed diagram given in figure 4. The lines a a' and b b' represent bodies showing rigidity at no speed and differ only in that the viscosity of the body b b' is the greater. The discontinuous line e' c' c d e represents fairly well the general characteristics of the results obtained with silicate mixtures. Hence, in order to include the substances named, it is necessary to modify the ideal assumption of a viscosity independent of shear to take account of the known rigidity at low shears.

As viscosity is defined as the ratio of the shear to the transverse velocity gradient, one may write

$$\eta=\frac{m}{D_n v}+n,$$

where m and n are constants, and D_n signifies a differentiation taken in a direction perpendicular to the velocity v. Using this value for the viscosity, the torque is given by the expression,[a]

$$\Gamma = A\omega + B,$$

where A is $[4\pi n r_1^2 r_2^2] \div [r_2^2 - r_1^2]$, and B is $[4\pi m r_1^2 r_2^2 \log r_2 \div r_1] \div [r_2^2 - r_1^2]$

Since this is the equation for the discontinuous curve in figure 4, the modified expression for viscosity is sufficient to account for the observed facts.

RELATIONS BETWEEN VISCOSITY, TEMPERATURE, AND COMPOSITION IN THE TERNARY SYSTEM.

The viscosity of a silicate within the ternary system CaO-Al_2O_3-SiO_2 is given by the expression[b]

$$\eta = f(L\ A\ T)$$

where T is the temperature, L the percentage of lime (CaO), and A the percentage of alumina (Al_2O_3). The experimental problem, therefore, was to determine the value of this function. The result of the experiments would be, say, a family of surfaces in three dimensions giving η as a function of L and A, with T equal to a constant parameter for each surface. Synthetic melts were made of mixtures representing appropriate values of L and A, and the viscosities of these were measured at temperatures ranging from near their melting point to an upper limit of 1,600° C. A construction of the surfaces obtained by plotting the results was attempted only for those parts of the fields of calcium metasilicate and gehlenite shown in figure 2. These surfaces are not of a simple nature; and their precise determination did not seem practicable without definite knowledge of the general relations to be expected. Results of experimental measurements on a relatively few compositions outside of the selected field, chosen with reference to the stability diagram shown in figure 1, were enough, when combined with results of the measurements made in this field, to permit the construction of the surfaces with satisfactory accuracy. The experimental methods and the results are described here.

---

[a] For uniform circular motion around an axis, $\Gamma = 2\pi r^3 \eta \frac{d\omega}{dr}$. Introducing the value of η above gives $\Gamma = 2\pi r^3 \left(\frac{m}{r \frac{d\omega}{dr}} + n \right) \frac{d\omega}{dr}$, which, integrated between the limits r_1 and r_2, becomes

$$\pi = \frac{\Gamma}{4\pi n} \left(\frac{r_2^2 - r_1^2}{r_1^2 r_2^2} - \frac{m}{n} \log \frac{r_2}{r_1} \right)$$

[b] The observed rigidity at low shears would demand the introduction of a fifth variable into this expression. As its effect, however, would not modify essentially the general relations considered, this further complication does not appear necessary here.

METHODS AND APPARATUS USED IN EXPERIMENTS.

PREPARATION OF SYNTHETIC MELTS.

The calcium oxide used was derived from Baker's analyzed calcium carbonate. Baker's analyzed aluminum oxide and Baker and Adamson's purified quartz were used. The quartz contained 0.016 per cent Fe_2O_3. The oxides were weighed out, thoroughly mixed, placed in a No. 2 Dixon plumbago crucible, and fused in a melter's gas furnace. The melt was then ground in an agate mortar to pass through a 100-mesh sieve. The ground sample was put in the Acheson graphite crucible used in the viscosity determinations. In all tests an analysis was made of the melt after the viscosity measurements. These analyses[a] showed the presence of an insoluble carbonaceous material, presumably graphite, to the extent of 0.04 to 0.14 per cent.

ANALYSES OF MELTS.

A number of analyses were made of the slag melts as prepared by the initial fusion, and on the same melts after the viscosity had been determined. A few of the results are given below.

TABLE 1.—*Results of analyses of slag before and after viscosity determinations.*

[Analyst, N. A. Sargent.]

Lab. No. of melt.	Constituent.	Content in slag— After preliminary fusion.	After first viscosity determination.	After second viscosity determination.
		Per cent.	*Per cent.*	*Per cent.*
M641	CaO	47.50	47.47	.....
	Al_2O_3	24.09	24.02	.....
	SiO_2	28.38	28.38	.....
M502	CaO	.....	25.06	25.08
	Al_2O_3	.....	12.92	13.12
	SiO_2	.....	61.82	61.50
M523	CaO	50.35	50.40	.....
	Al_2O_3	41.40	41.42	.....
	SiO_2	7.62	7.78	.....

FURNACE AND ACCESSORIES.

The methods of measurement, the electric furnace, and the viscosity apparatus are essentially those described in previous reports.[b] Drawings of the furnace and its various parts are shown in Plate I.

[a] The analyses were made by N. A. Sargent, junior analytical chemist of the Bureau of Mines, according to the methods given by W. F. Hillebrand in The analysis of silicate and carbonate rocks, Bull. 422, U. S. Geol. Survey, 1910, 239 pp.

[b] Feild, A. L., A method for measuring the viscosity of blast-furnace slag at high temperatures, Tech. Paper 157, Bureau of Mines, 1916, 29 pp.; The viscosity of blast-furnace slag, Am. Inst. Min. Eng. Bull. 122, February, 1917, pp. 307–332.

Data on parts shown in Plate I.

Piece No.	Name of piece.	Material.	Number required.
1	Oil-well casing, 14 inches in outside diameter	Cast iron	1
2	Flange	do	2
3	do	do	4
4	Leg	Round iron	3
5	Support	Iron	3
6	Floor plate	Sheet iron	1
7	Guide	Cast iron	6
8	Rod	Iron	6
9	do	do	3
10	Support	Strap iron	2
11	Adjusting screw	Iron rod	3
12	Bracket for upper bearing	Cast iron	1
13	Bracket for lower bearing	do	1
14	Upper bearing	Brass	1
15	Lower bearing	do	1
16	Hexagonal nut	do	1
17	Bracket strap	Strap iron	2
18	Shaft and pulley	As shown	1
19	Tubes	Alundum	As shown.
20	Electrode	Graphite	1
21	do	do	1
22	Terminal bracket	As shown	1
23	Set-screw nut	Soft iron	2
24	Set-screw washer	Steel	2

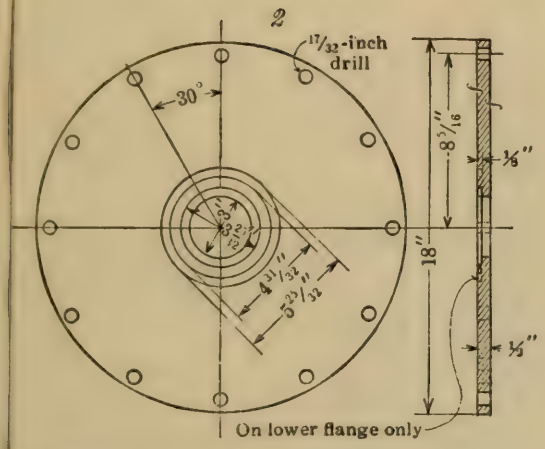
In order to make continuous measurements with a number of slags without waiting for the furnace to cool the graphite crucible with its supporting rod, shaft, and bearings was given enough vertical play to permit lowering the crucible below the bottom of the furnace shell. While in position outside of the furnace the shaft, with the hot crucible, could be removed from the shaft bearings and a new crucible and charge substituted.

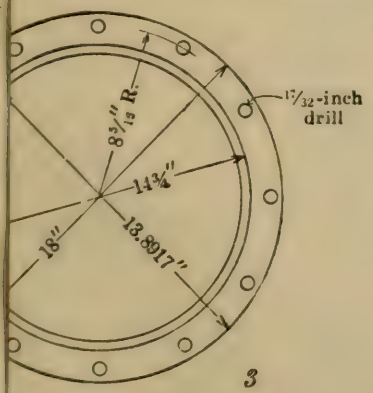
The Holborn-Kurlbaum optical pyrometer used in measuring the temperature of the slag within the crucible was sighted horizontally on an absorption prism placed over the opening in the top of the furnace and inclined at an angle of 45°, so that the light rays emerging from the furnace vertically were reflected horizontally into the pyrometer. By this device the optical pyrometer and the telescope used in reading scale deflections were placed side by side, so that the temperature and the deflection, which is proportional to the viscosity, could be read in rapid succession by the same experimenter without changing his position.

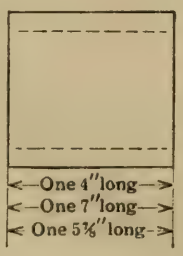
TEMPERATURE MEASUREMENTS.

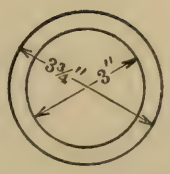
The current in the pyrometer lamp was measured by means of a standard manganin shunt and a Weston standard cell.

The Holborn-Kurlbaum pyrometer, as constructed by the manufacturer, was equipped with an ordinary milliammeter. In addition









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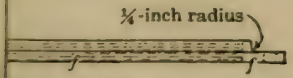

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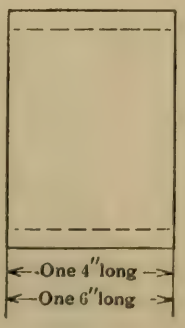

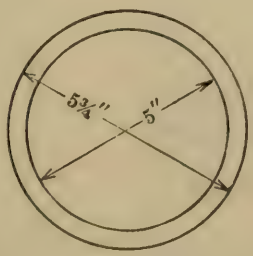

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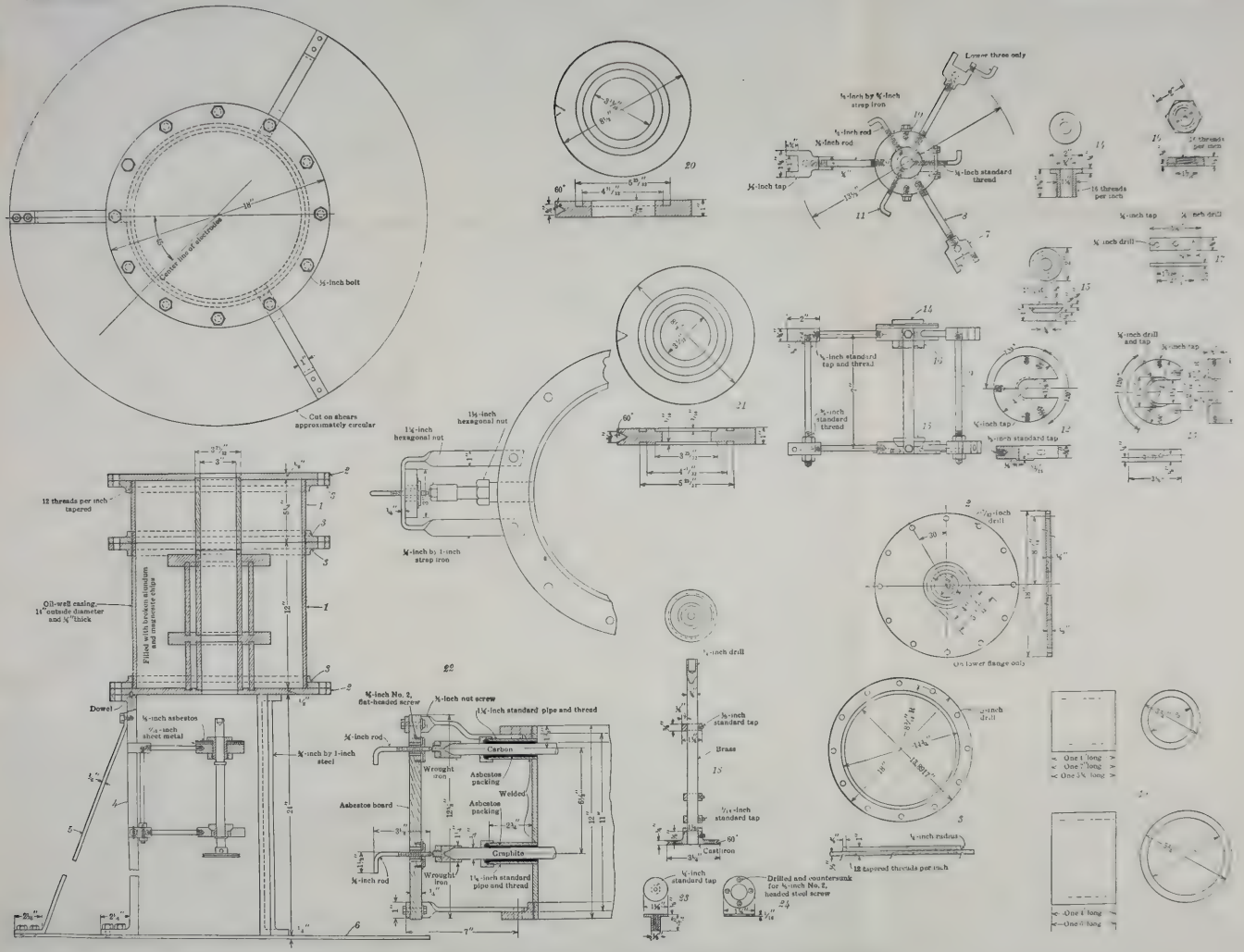

DETAILS OF ELECTRIC FURNACE USED IN TEMPERATURE-VISCOSITY DETERMINATIONS.

to the fact that a swinging-coil instrument is untrustworthy where great accuracy is desired, it was found that the current of the pyrometer lamp could be regulated by the eye to correspond to the temperature of the furnace more accurately than readings could be made on the milliammeter. Hence the potentiometer method was adopted.

The pyrometer lamp and absorption prism were calibrated against a platinum platinum-rhodium thermocouple bearing a Bureau of Standards certificate in the usual "black-body" platinum resistance furnace.

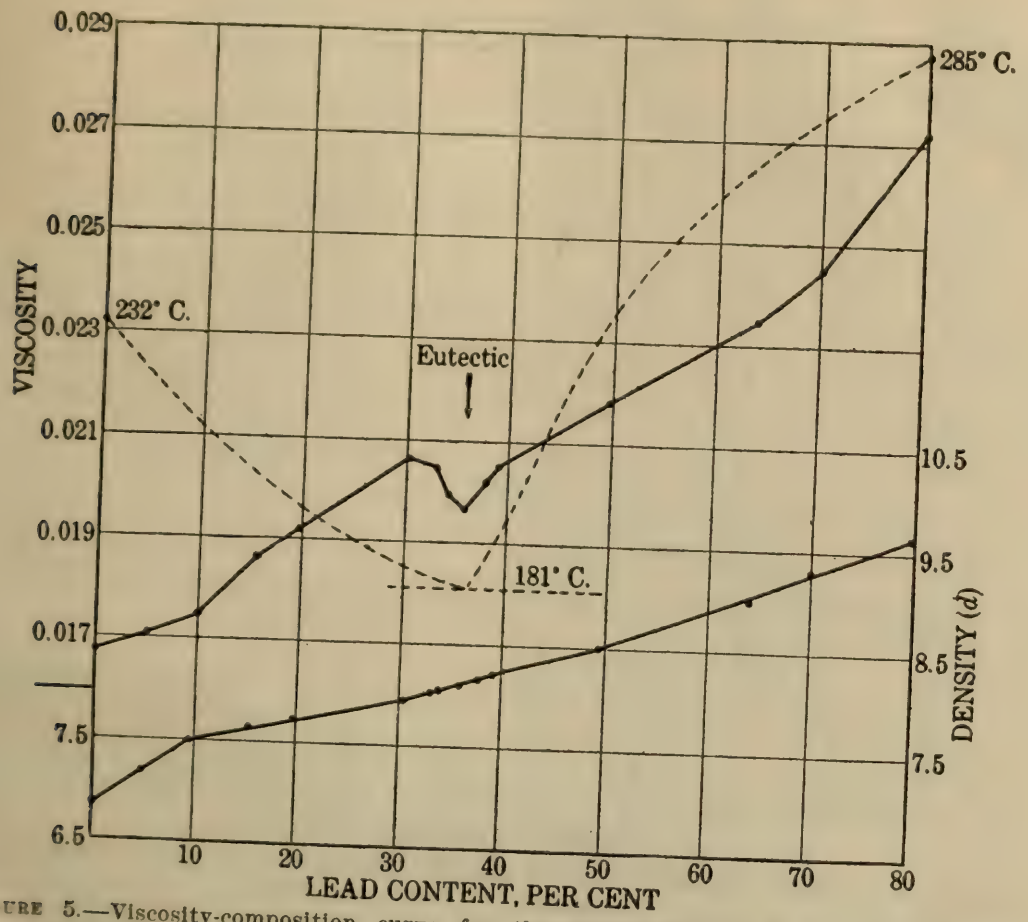

FIGURE 5.—Viscosity-composition curve for the binary system Pb-Sn. After Plüss.
------- melting curve after Degens.

VISCOSITY MEASUREMENTS.

The melt was contained in an Acheson graphite crucible, about 4.5 cm. in diameter, which was rotated at a measured speed. The torque on a graphite rod, about 1.3 cm. in diameter, suspended in the axis of the crucible from a steel ribbon, was measured by observing the torsion produced in the ribbon. From the observed moment of inertia, time of swing, and the torsion of the suspended system, the torque on the central rod could be computed.

The length of inner cylinder that was immersed in the melted slag could be readily measured by making the inner cylinder and the

crucible the terminals of an open battery circuit containing a galvanometer, and noting the position at which the small current flowing through the melt was made or broken.

The magnitude of the small torque exerted by the liquid on the end of the inner cylinder was verified by continuous measurements on the cylinder as it was withdrawn gradually from the liquid.

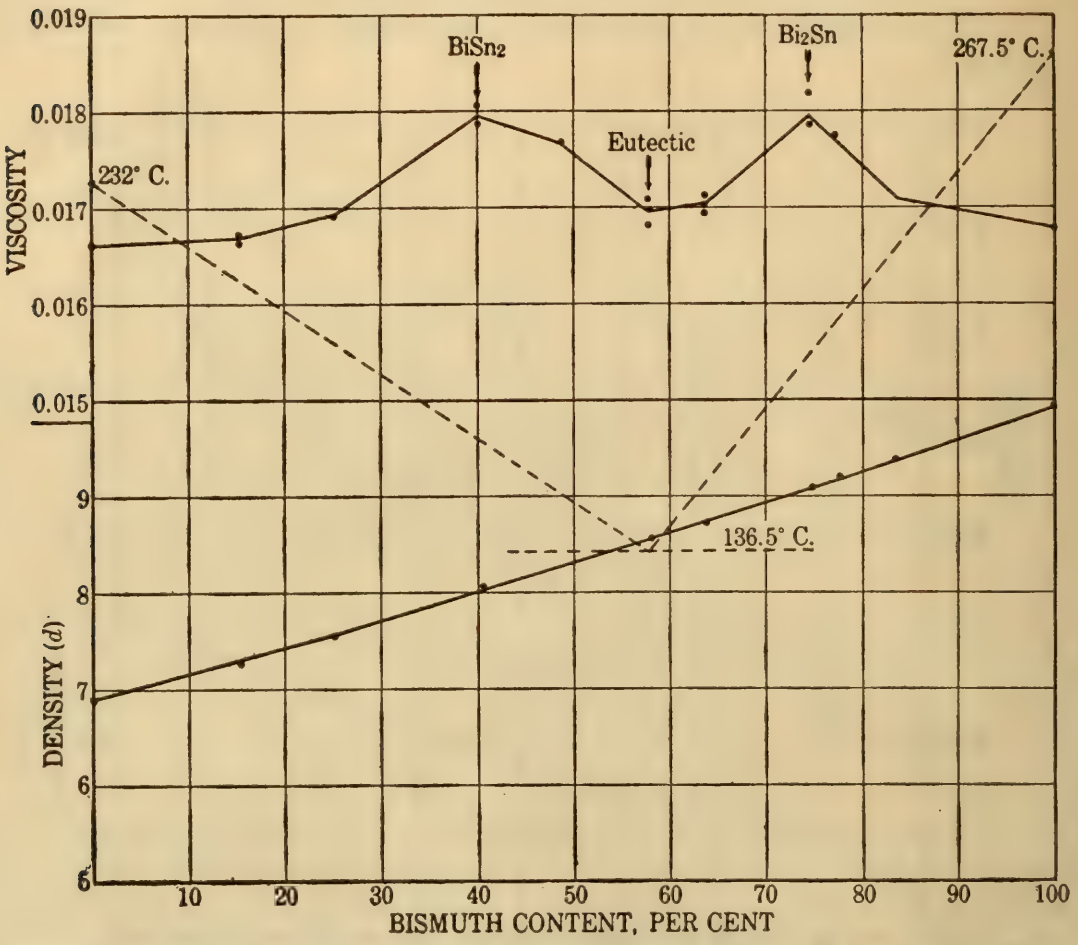

FIGURE 6.—Viscosity-composition curve for the binary system Bi-Sn. After Plüss. ----- melting curve after Lepkowski.

RESULTS OF EXPERIMENTS AND DISCUSSION OF RESULTS.

VISCOSITY OF BINARY SYSTEMS.

Plüss[a] observed that in the binary alloys Pb-Sn and Bi-Sn there is a minimum in the viscosity-composition curve at the eutectic composition. The experimental data are shown for these two binary systems in figures 5 and 6. The same property of minimum viscosity at the eutectic was observed by Goodwin and Mailey[b] in fused mix-

[a] Plüss, M., Zur Kenntnis der Viskosität und Dichte geschmolzen Metalle und Legierungen: Ztschr. Anorg. Chem., Bd. 93, 1915, pp. 1–44.

[b] Goodwin, H. M., and Mailey, R. D., On the density, electrical conductivity, and viscosity of fused salts and their mixtures: Phys. Rev., vol. 25, 1907, pp. 469–489; vol. 26, 1908, pp. 28–60.

tures of sodium and potassium nitrates, although attention was not called to the fact that this minimum corresponded to the eutectic composition.

THE BINARY SYSTEM CALCIUM METASILICATE-GEHLENITE.

Figure 7 shows viscosities at 1350°, 1400°, 1500°, and 1600° C. over a part of the binary system calcium metasilicate-gehlenite. As is

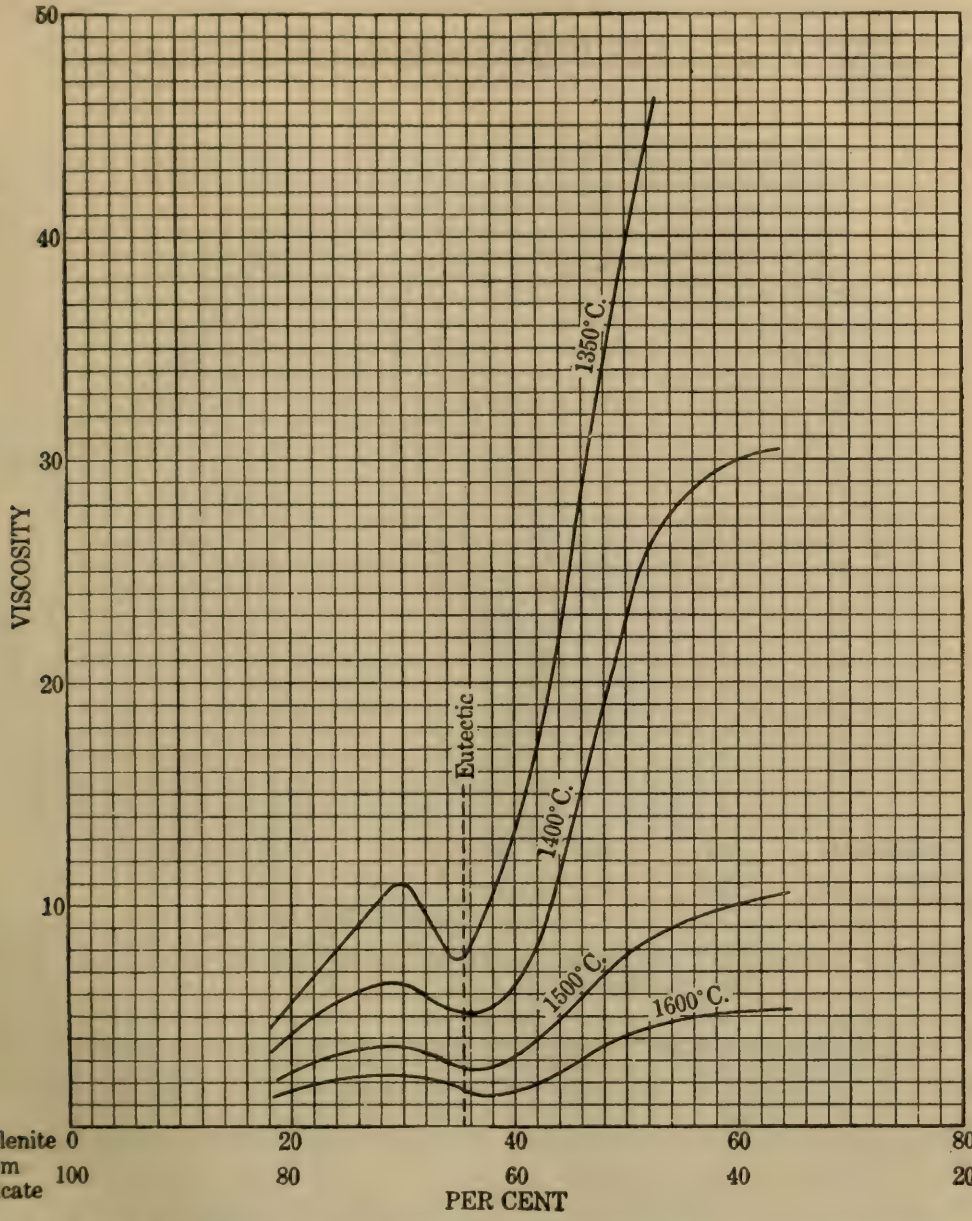

FIGURE 7.—Profiles of isothermal viscosity surfaces along the calcium metasilicate-gehlenite binary system.

seen, the eutectic shows a minimum viscosity similar to that observed in the binary alloys by Plüss. A maximum occurs at about 30 per cent gehlenite, which is similar in its character to that observed by Plüss and attributed by him to the existence of intermetallic com-

pounds. Although such a deduction might be made in this work, leading to a hypothetical compound between calcium metasilicate and gehlenite in the liquid state, such an assumption seems hardly justified.

In figure 8 viscosities are plotted for the system at the saturation temperature and at 50° and 100° C. superheat. The curves show that at its melting point the binary eutectic exhibits maximum viscosity when compared with contiguous mixtures at their saturation temperatures, and that this rule holds true at higher temperatures.

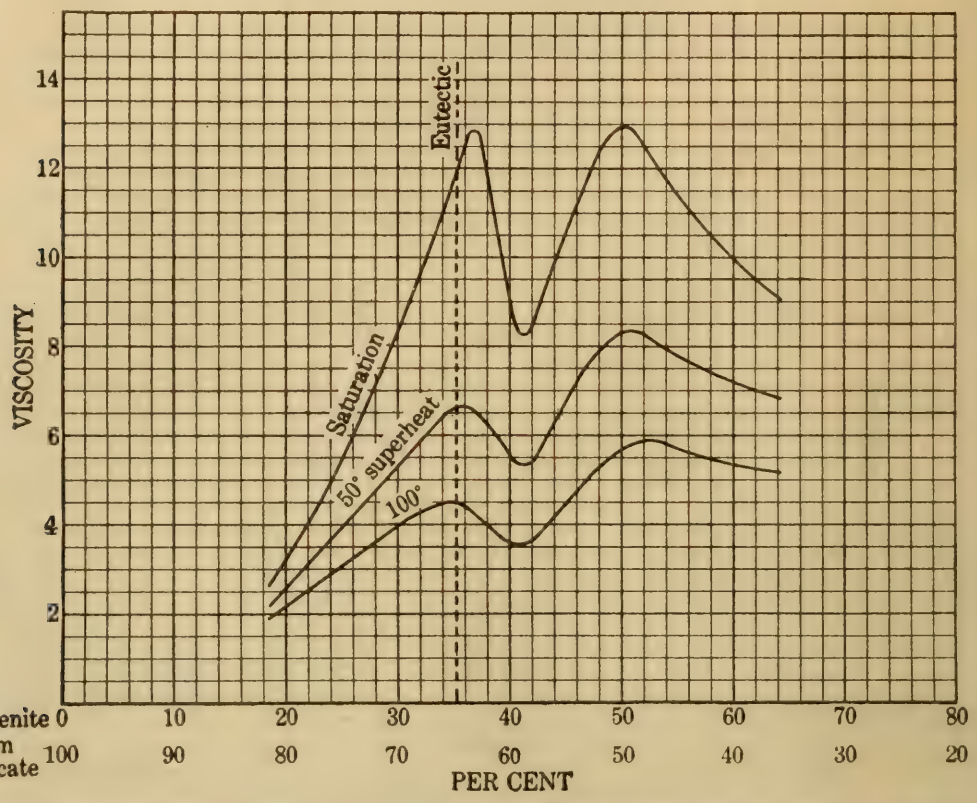

FIGURE 8.—Viscosities in the binary system calcium metasilicate-gehlenite at the saturation temperature and at 50° and 100° C. superheat.

Although the entire binary system was not investigated, it would seem that, starting with either pure component, the isothermal viscosity curve increases first to a maximum and then decreases toward the eutectic.

VISCOSITIES AT QUINTUPLE POINTS OF THE TERNARY SYSTEM.

Viscosity measurements were made of mixtures representing seven quintuple points of the ternary system, corresponding to points *2*, *5*, *6*, *7*, *8*, *14*, and *20* as given in Rankin and Wright's composition diagram (fig. 1). The temperature-viscosity curves for these mixtures are shown in figure 9. The composition of these mixtures in terms

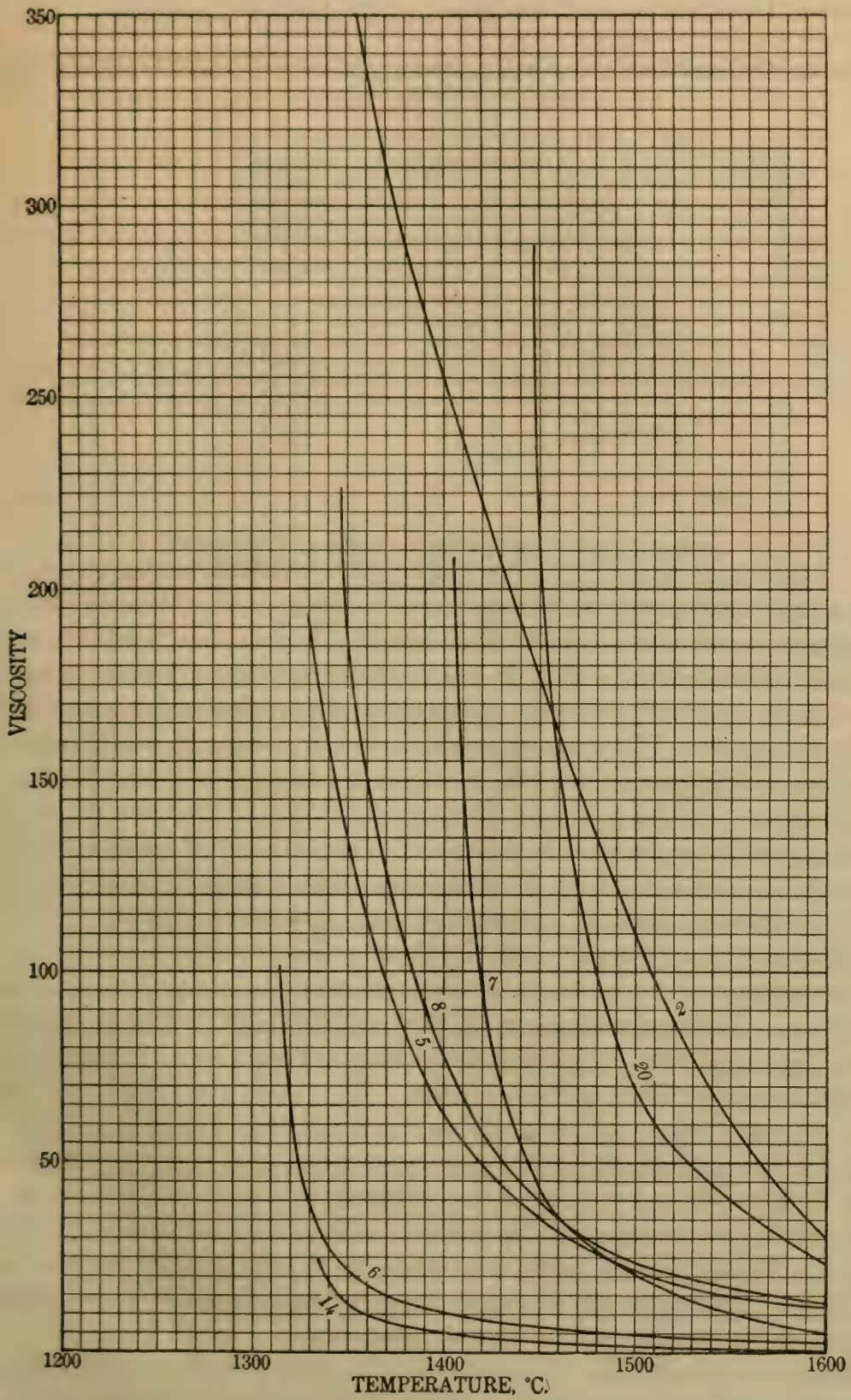

FIGURE 9.—Temperature-viscosity curves of quintuple points at which viscosity measurements were made (numerals same as on fig. 1).

of the original components, together with their melting points as observed by those writers, are given in the table following.

TABLE 2.—*Compositions and melting points of mixtures representing quintuple points.*

Point No.	Composition of melt.			Melting point according to Rankin and Wright.
	CaO.	Al_2O_3.	SiO_2.	
	Per ct.	*Per ct.*	*Per ct.*	° *C.*
2...	23.25	14.75	62	1,170±5
5...	38	20	42	1,265±5
6...	47.2	11.8	41	1,310±5
7...	29.2	39	31.8	1,380±5
8 [a]	49	14.4	36.6	1,415±5
14..	49.5	43.7	6.8	1,335±5
20 [a]	48.7	39.3	12	1,430±5

[a] Points *8* and *20* do not represent eutectics; the others represent ternary eutectics.

CRYSTALLIZATION IN THE TERNARY SYSTEM.

As has been previously stated, the viscosity of silicates usually increases continuously with decreasing temperature, and becomes infinite asymptotically to the melting temperature. Hence crystallization in a ternary eutectic seemingly can proceed with great difficulty, if at all. If crystallization does not occur, it would not be possible to find more than two solid phases in any given melt within the system. In the work of Rankin and Wright the occurrence of three crystalline phases is recorded for the mixtures represented by points *12*, *14*, *15*, *13*, and *6*. Of these five quintuple points, *12*, *14*, and *15* represent ternary eutectics, whereas *13* and *6* do not.

Of the five quintuple points investigated by them, two, *6* and *14*, were among the seven on which viscosity measurements are here reported. Reference to figure 9 shows that these two alone do not obey the usual rule of possessing a temperature-viscosity curve that is continuous at the melting point. The fact that each of these two curves is discontinuous shows that the liquid would not have infinite viscosity at the melting temperature, and hence crystallization should proceed without great difficulty.

In order to investigate the matter more fully, an optical examination of a number of melts was made by W. H. Fry, of the Bureau of Soils. The data given below were included in his unpublished report on the results of the examination.

Melts corresponding to points *2*, *4*, *5*, and *7* were glasses, being isotropic and having a decided conchoidal fracture. A minute trace, however, of doubly refracting material was noted in each melt, being less than 0.01 per cent, and probably much less than 0.001 per

cent. The spherulitic structure of some of this doubly refracting material, in melts representing points *2*, *5*, and *7*, suggests incipient crystallization. The samples were colorless, or nearly so, by transmitted light, under the microscope; and all showed the presence of minute inclusions, presumably graphite particles.

For point *14*, the isotropic material constituted roughly something more than three-fourths of the sample. The doubly refracting material took the form of incipiently crystallized (dendritic) and of extremely minute particles, which optically were fairly homogeneous.

Until further evidence is adduced, it is not possible conclusively to state that, within the meaning of the phase rule, complete equilibrium is ever attained by purely thermal means in a typical silicate, such as point *2* or point *5*, where the viscosity shows no discontinuity at the melting point.

VISCOSITIES OF SILICATES LYING ALONG THE BOUNDARY CURVES.

Viscosity measurements were made of compositions lying on the boundary curves between the fields of calcium metasilicate and of anorthite; calcium metasilicate and gehlenite; gehlenite and anorthite; and calcium orthosilicate and gehlenite. The viscosities for these four boundaries at temperatures of 1400°, 1500°, and 1600° C. are shown, respectively, in figures 10, 11, 12, and 13.

Each of the curves terminates at a quintuple point which represents a eutectic, and includes, between these two ternary eutectics, the binary eutectic between those two compounds whose stability fields it limits. In the boundary curve between calcium orthosilicate and gehlenite (fig. 13) there are, in addition to the two terminal quintuple points that represent eutectics, two quintuple points that are not eutectics. These latter points, *8* and *20*, are the points where gehlenite, α and β calcium orthosilicate are in equilibrium with their melt. The field of stability of the β form of the orthosilicate, as determined by Rankin and Wright, appears as the two discreet areas *3 4 8* and *20 13 14 15 19* in figure 1. The viscosities of the two mixtures represented by points *8* and *20* are much higher, for a given temperature, than has been observed for any composition lying in this part of the system. In fact, at 1,460° C. the viscosity for the mixture represented by point *20* is equal to that of the mixture represented by point *2*, containing 62 per cent SiO_2. The existence, then, of the molecular aggregate identified with the β form is responsible in some way for this excessive viscosity.

The viscosity relations for each of these boundary curves exhibit general characteristics in common. In each curve the viscosity in-

creases from a minimum at a binary eutectic to a maximum at a quintuple point. Point *5* is a common terminus in three of the four boundary curves, as shown in figures 10, 11, and 12. The general form of the isothermal viscosity surfaces can be readily visualized by reference to these figures and to figure 1. The viscosity at this point

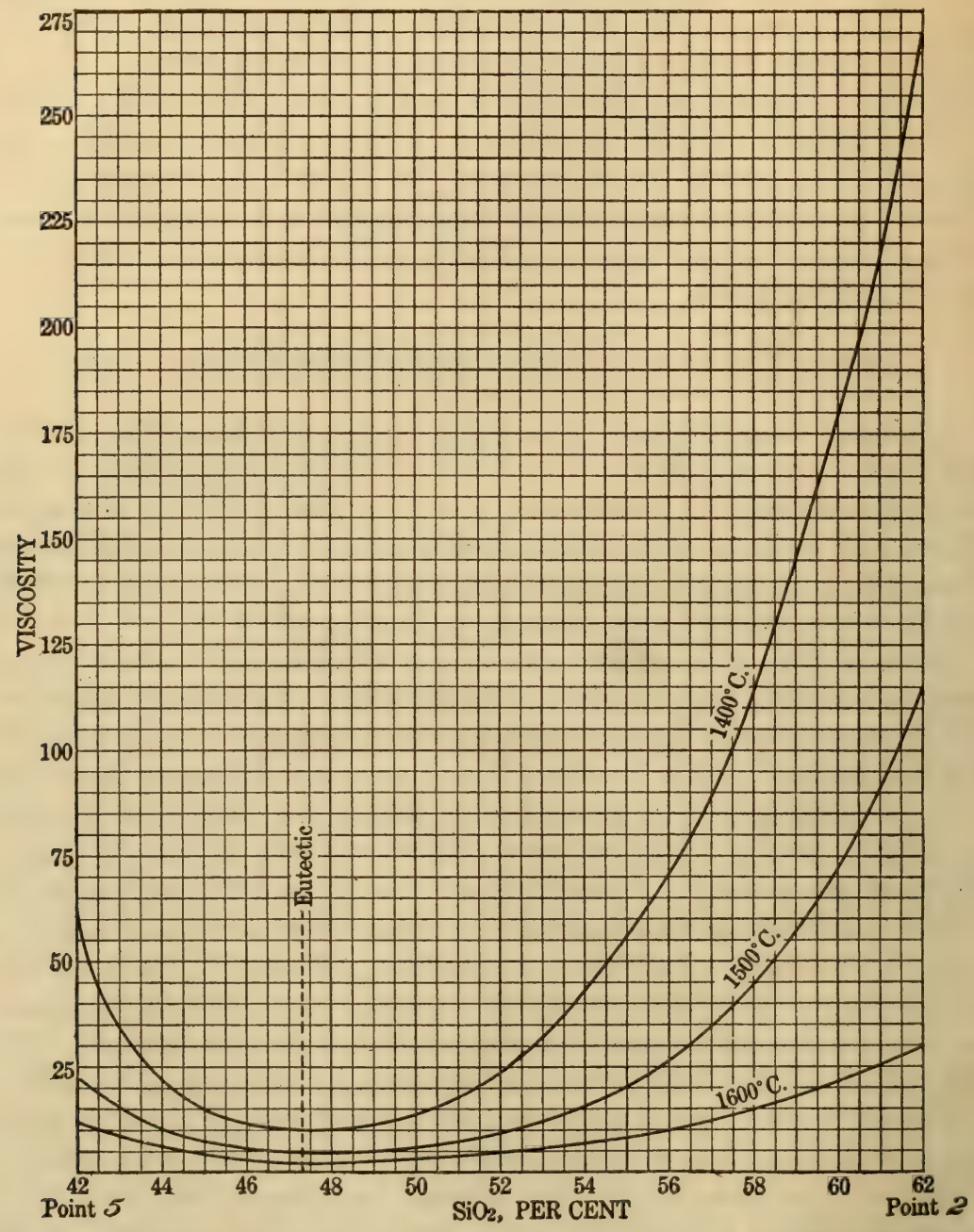

FIGURE 10.—Profiles of isothermal viscosity surfaces along the calcium metasilicate-anorthite boundary curve.

must be a maximum, therefore, for all variations in composition. In the same way the form of the viscosity surface in the neighborhood of the metasilicate-gehlenite binary eutectic can be visualized by reference to figures 7 and 11, being respectively the binary system

and the boundary curve that intersects it at this composition. The viscosity surface clearly shows here a minimum with respect to all variations in composition.

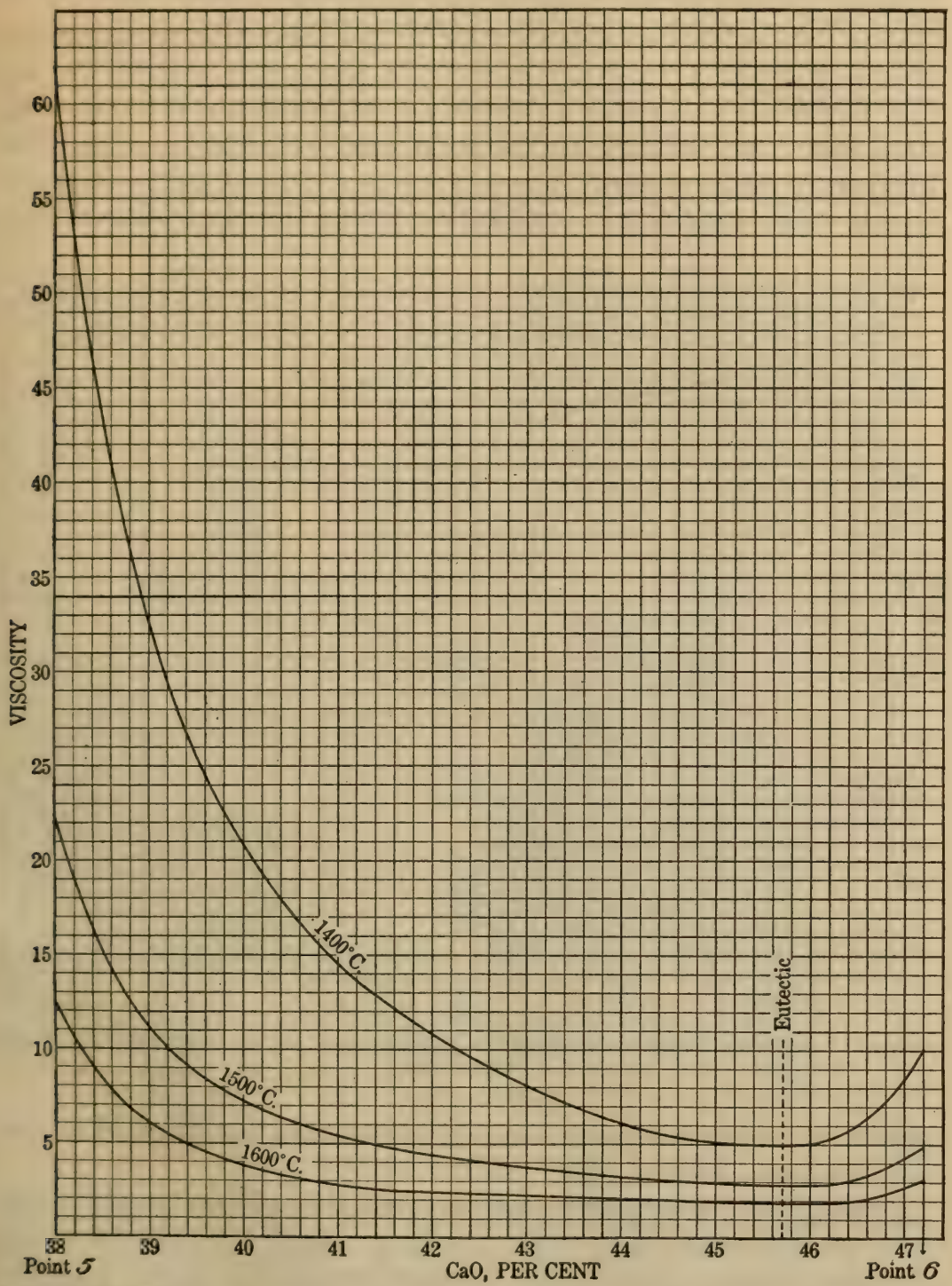

FIGURE 11.—Profiles of isothermal viscosity surfaces along the calcium metasilicate-gehlenite boundary curve.

MELTING POINT.

As regards mixtures of solids, particularly silicates, attempts have been made, by studying their structure and mechanical behavior, to

assign to each composition a melting point. In a chemical element or chemical compound there is fortunately no possibility of confusion in regard to what this point is. When two or more compounds are considered together, however, confusion has arisen.

It is impossible logically to refer to the saturation temperatures of a mixture as a "melting point." In the first place, the crystal that forms has undergone a change, not from the liquid to the solid state, but from solution to the solid state—that is, precipitation. The term "melting point" has so long been defined as the temperature at which a solid is in equilibrium with a liquid of its own com-

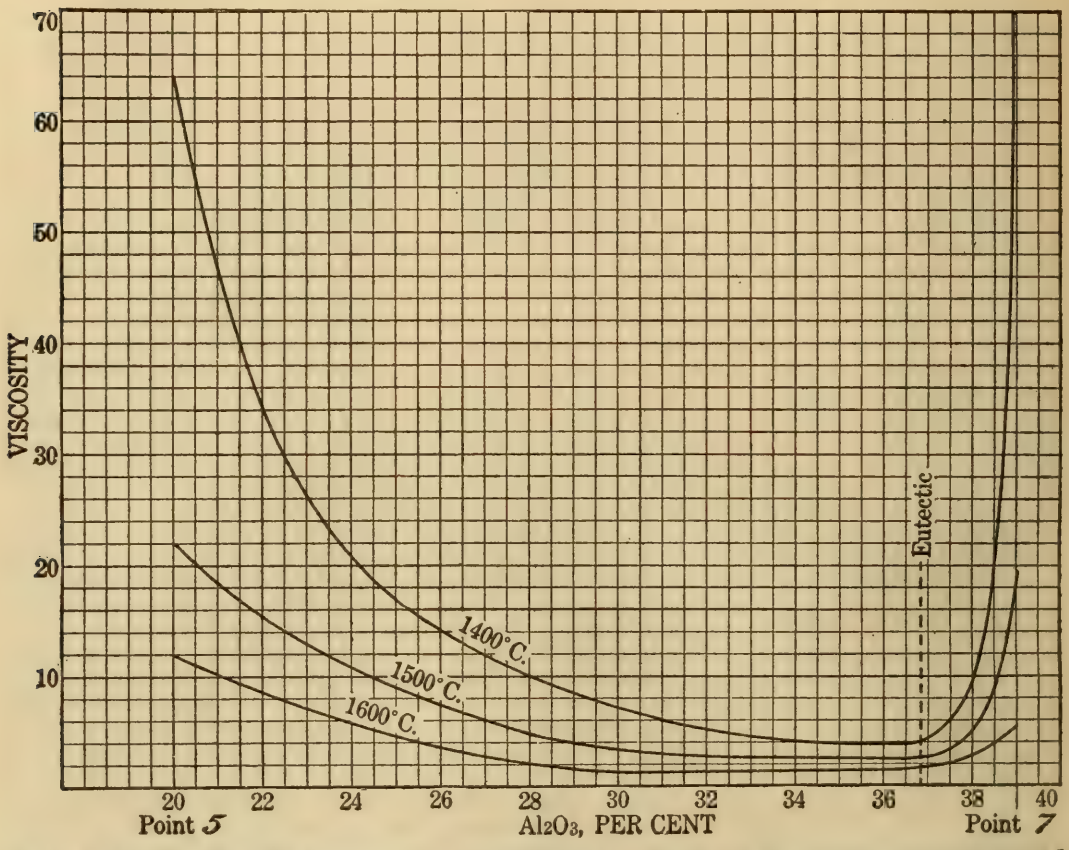

FIGURE 12.—Profiles of isothermal viscosity surfaces along the anorthite-gehlenite boundary curve.

position that extending the meaning to cover the condition of saturation has never seemed wise.

Aside from the saturation temperature, the only temperature that can be associated with the term "melting point" for mixtures within a ternary system will be the temperature at the staple quintuple point. This temperature agrees with the physical definition of melting point, as already given, and there seems to be no sound objection to its use in this sense. Mixtures of the three compounds therefore can have only one melting point, which does not depend on the relative proportions of the compounds present. Observations of the

deformation of heated substances, and of temperatures described as those at which the substance becomes "visibly fluid," obviously refer to the temperature at which the viscosity of the heterogeneous system reaches some indefinite value depending upon the conditions of the experiment. Such data not only have no scientific meaning but give no definite information concerning purely mechanical behavior under conditions other than those of the experiment.

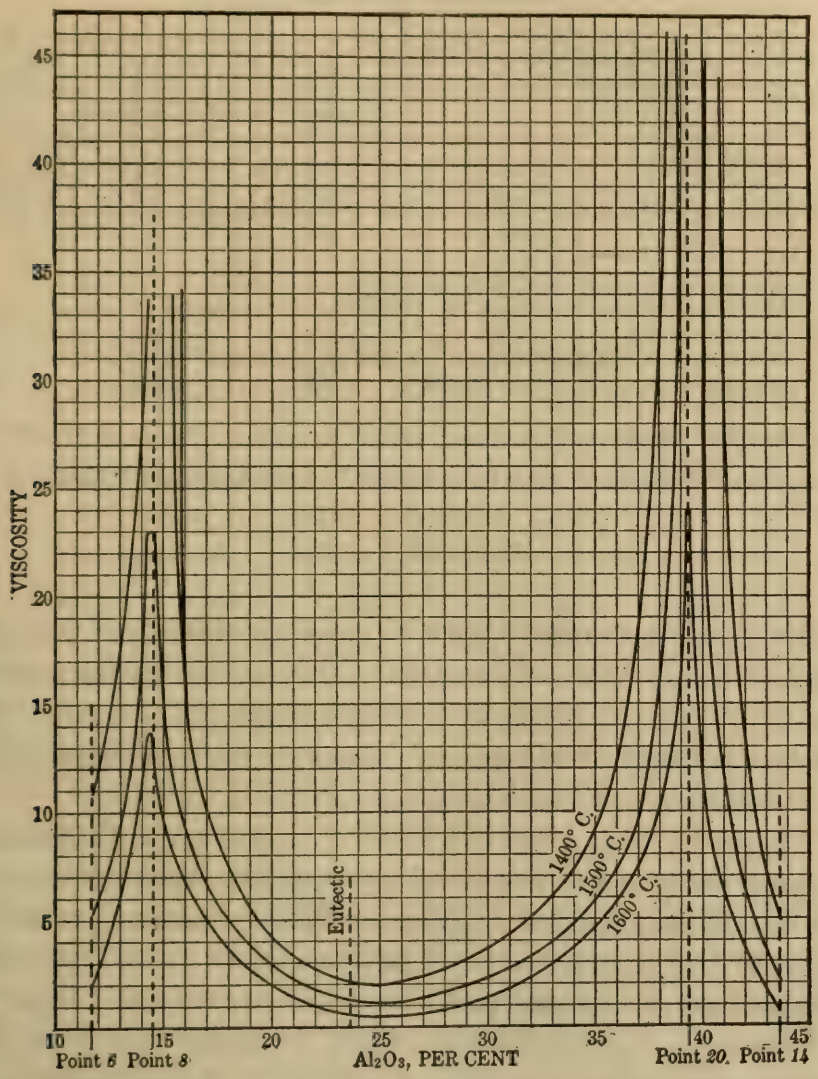

FIGURE 13.—Profiles of isothermal viscosity surfaces along the calcium orthosilicate-gehlenite boundary curve.

The reason for the confusion that has arisen in regard to the so-called "melting point" of silicate mixtures will be readily seen from a study of the actual viscosity measurements given herein. It will be more convenient, perhaps, to consider the reciprocal of the viscosity, or what is usually termed the fluidity. If the temperature-viscosity relations of the compositions that correspond to the quintuple points shown in figure 9 be represented in terms of fluidity upon the temperature-fluidity diagram, the resulting curve of each

will be more or less a straight line convex to the temperature axis, the fluidity increasing with increasing temperature. These curves do not appear to belong to any simple family of mathematical curves, but within the range of measurement it is possible to express the temperature as a power series of the fluidity. For point *2* it is found that the expression

$$T=1167+737\frac{\phi}{100}-445\left(\frac{\phi}{100}\right)^2$$

agrees with the experimental values with a mean deviation of 5.5° C. over a range of viscosity from 100 to 2,000. If it be assumed that the expression holds for a range of fluidity 5 per cent greater—that is, as far as ϕ equals zero—the temperature corresponding to zero fluidity would be 1167° C. The value given by Rankin and Wright [a], as shown in Table 2, is 1170° C. ± 5°.

Similarly, for point *5*, the expression

$$T=1269+132\frac{\phi}{100}-38\left(\frac{\phi}{100}\right)^2+4.9\left(\frac{\phi}{100}\right)^3$$

agrees with the observed values with a mean deviation of 4.4° C. over a range of viscosity from 33 to 200. For point *7* the equation

$$T=1388+35.5\frac{\phi}{100}-2.9\left(\frac{\phi}{100}\right)^2$$

agrees with the observations with a mean deviation of 1.6° C. over a range of viscosity from 33 to 166. The temperatures corresponding to zero fluidity in these two instances are 1269° and 1388° C., respectively. Values obtained by Rankin and Wright, given in Table 2, are 1265° ± 5° and 1380° ± 5°.

The evidence is, then, that the fluidity decreases with falling temperature according to the relations given in the equations above, and therefore the temperature at which the fluidity becomes zero is a perfectly definite temperature. It is impossible to attach any meaning to the suggestion that these silicates have a melting "interval," or melting "range." The melting point is the point at which the mixtures become solid—that is, when the fluidity becomes zero. If the fluidity curve does not obey the experimental equations given above at fluidities lower than those measured, it must become zero at some point or approach zero asymptotically. If the point is other than that given, this means merely that the melting points as determined by Rankin and Wright and by the writers of this report are in error, but the point is not therefore less definite. If the fluidity curve approaches the temperature axis asymptotically, the fluidity never becomes zero, and therefore the substance has no melting point. In

[a] Rankin, C. A., and Wright, F. E., place cited.

any of the supposed examples no possible meaning can be assigned to the expression "melting interval."

VISCOSITIES WITHIN THE STABILITY FIELDS.

As has been explained, the particular problem for whose solution this investigation was undertaken is the determination of the temperature-viscosity relations for the compositions of silicates lying within the field shown in figure 2. It was thought that these results would prove more useful if presented in the form of a table giving the viscosities at various temperatures for fixed percentages of the constituent oxides CaO, Al_2O_3, and SiO_2. Such a set of tables is given in Technical Paper 187.[a] In that publication the magnitude of the possible experimental error was not discussed.

As such data are urgently needed in the industries concerned and have not been published hitherto, it seemed desirable to publish the results of the investigation even if a considerable number of the results were somewhat in error. Moreover, from the nature of the experiments it is almost impossible to determine from the data the degree of accuracy obtained. Each of the experimentally observed quantities was read correctly within a fraction of a per cent, but, owing to the slowness with which the melts had to be handled in order to assure a reasonable approach to equilibrium, to have set the precision of the observations as a standard of absolute accuracy for the whole field of investigation would have unduly prolonged the research. However, it can be said with certainty that in none of the practical applications of these measurements under present industrial conditions could the errors prove large enough to be of the slightest consequence.

There is no need of duplicating these tables in the present paper. In order to give some idea of the general nature of the isothermal viscosity surfaces, profiles of these surfaces at 1450° C. for alumina percentages of 7, 10, 15, 18, and 21 are shown in figures 14 and 15. In figure 14, for 7 per cent Al_2O_3, the letters *a*, *f*, and *b* refer to compositions corresponding to the same letters as shown in figure 2. The boundary curve between the fields of calcium metasilicate and akermannite occurs at *a*; *f* lies on the boundary curve of the binary system calcium metasilicate-gehlenite; and *b* on that of the binary system calcium metasilicate-anorthite. For the curve representing 10 per cent Al_2O_3 (fig. 14) the letters *a'*, *f'*, and *b'* show the intersection of the same curves, respectively. This part of the calcium metasilicate field is characterized by a relatively low viscosity.

[a] Feild, A. L., and Royster, P. H., Slag viscosity tables for blast-furnace work: Tech. Paper 187, Bureau of Mines, 1917, 38 pp.

Within the area *6 0 f a* (fig. 2) the primary phase crystallizing from the melt is observed to separate from the rather fluid melt and to float on top, so that care must be taken that the solidified mass does not attach itself to the central cylinder or the outer crucible of the viscosity apparatus. This separation of crystals has been observed for no melts outside of this particular region.

The curve for 15 per cent Al_2O_3 (fig. 15) starts on the left at the metasilicate-anorthite binary system at 37 per cent CaO and passes from the metasilicate field into the gehlenite field at 43.5 per cent CaO, the viscosity decreasing to a minimum at 45 per cent CaO and

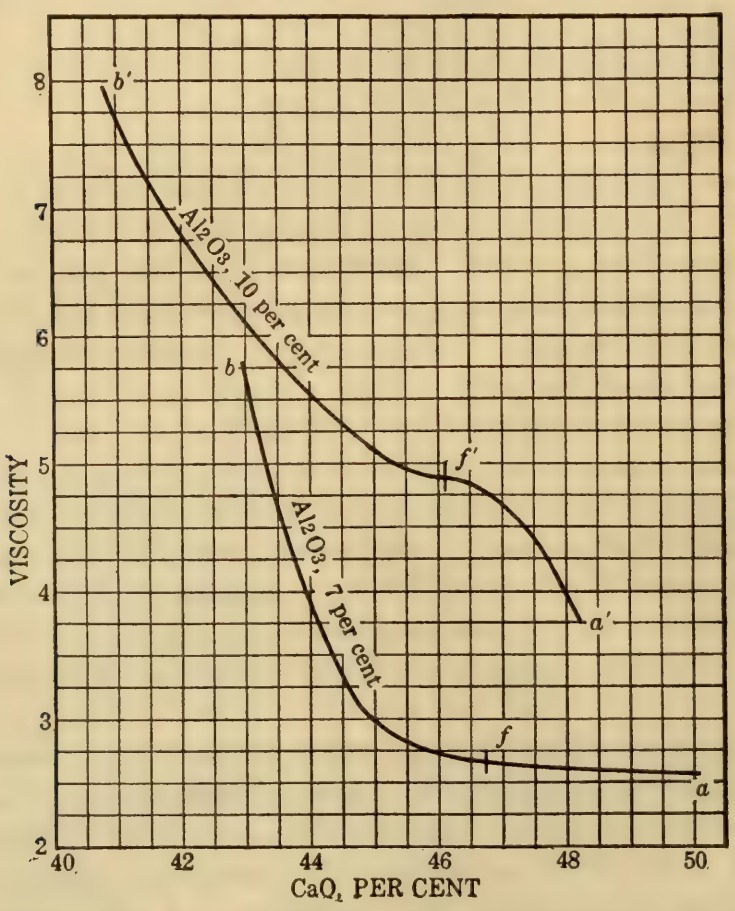

FIGURE 14.—Profiles of the isothermal viscosity surfaces at 1450° C. for mixtures containing 7 and 10 per cent Al_2O_3.

then increasing rapidly with increasing lime to the boundary of the gehlenite field at 49 per cent CaO. This latter terminus of the curve, as can be seen in figure 2, corresponds to the composition 36 per cent SiO_2, 15 per cent Al_2O_3, and 49 per cent CaO, and lies close to the quintuple point *8*. The high viscosity of compositions lying in or near the stability field of β calcium orthosilicate has been already noted.

The curve for 18 per cent Al_2O_3, as will be seen by reference to figure 15, starts at a minimum at 34.5 per cent CaO (just out-

side the area shown by fig. 2) at a composition corresponding to the eutectic between metasilicate and anorthite, increases to a maximum at the point representing the intersection of the metasilicate-gehlenite binary system (44.5 per cent CaO), and then decreases to its terminus at the gehlenite-orthosilicate boundary at 49.3 per cent CaO. At 37.5 per cent CaO the curve for 21 per cent Al_2O_3 begins with a high viscosity because of its proximity to point *5*, decreases with increasing lime content to a point flexure at the meta-

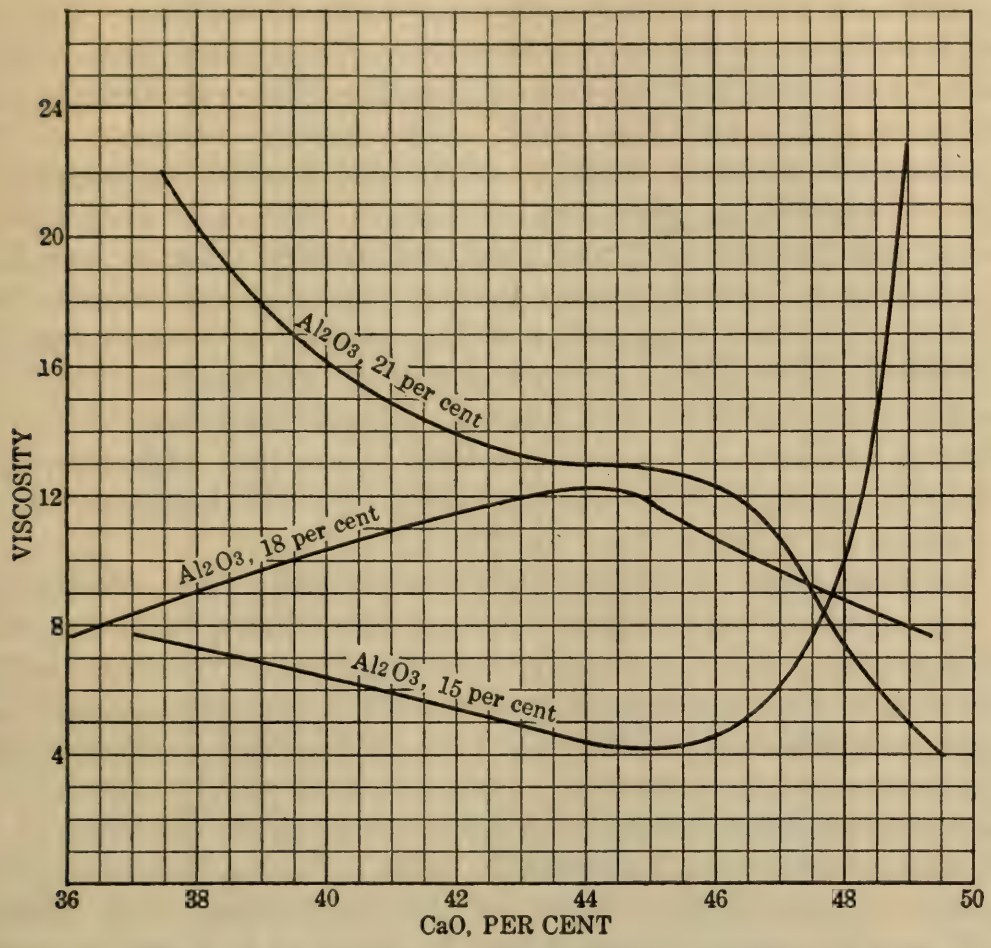

FIGURE 15.—Profiles of the isothermal viscosity surfaces at 1450° C. for mixtures containing 15, 18, and 21 per cent Al_2O_3.

silicate-gehlenite binary system at 44 per cent CaO, and then decreases more rapidly to the gehlenite-orthosilicate boundary.

From the preceding statements it may be seen that the viscosity surfaces are not of a simple nature when a single temperature is considered, whereas the form of these surfaces is greatly dependent upon the particular temperature chosen.

IMPORTANT CONCLUSIONS FROM RESULTS.

The experimental data described herein was the result of an investigation, in which no attempt was made to cover the entire system CaO-Al_2O_3-SiO_2, but was obtained with particular reference to a

specific industrial problem. In the beginning of the research the number and the composition of the compounds occurring in dry melts and the range of compositions within which these solid compounds are stable was known from the diagram of Rankin and Wright (fig. 1). However, the results obtained are enough to point strongly to the conclusion that by measurements of the viscosity of these silicates in the liquid state alone it would be possible to establish the existence of the compounds within the ternary system and to determine more or less closely their fields of stability. The viscosity surfaces, as far as they have been investigated here, show a certain number of maxima and minima, the former occurring at the quintuple points and the latter at the binary eutectics. As the boundary line between two fields of stability (except for compounds that are unstable at their melting points) terminates at quintuple points and includes one, and only one, binary eutectic, boundary curves may be drawn to pass through the observed maxima and minima. It is not suggested that this method of determining the stability fields would be convenient or even practicable. However, the following conclusion is of interest: If from the measurement of a physical property of a liquid the field of stability of a compound can be determined, it follows inevitably that the compound exists as such in the liquid state.

The great effect of the molecular composition of the constituents of the molten silicate mixtures having been shown, it is obviously futile to search for a general relation between the viscosity and the composition as expressed in terms of the component oxides. Attempts to establish some such rule from more or less qualitative data have been usual, it is true. For example, it is widely believed that increasing the silica content of a molten magma has the effect of increasing its viscosity. Reference to figure 10 shows that as the SiO_2 content is raised from 42 to 48 per cent the viscosity falls from 67 to 10, at the constant temperature of 1,400° C. It might be profitable, however, to determine whether some underlying fact may not be responsible for the general acceptance of such a rule.

As it is obviously impossible to compare the viscosity of silicate mixtures without reference to their position upon the stability diagram (fig. 1, p. 6), the most promising course would be to compare the oxide content and the viscosities of the mixtures represented by the various quintuple points and the binary eutectics. It will be seen from figure 9 that at 1450° C. the order of the quintuple points arranged in order of decreasing viscosity is *20*, *2*, *7*, *8*, *5*, *6*, *14*. At 1500° C., however, the order is *2*, *20*, *8*, *5*, *7*, *6*, *14*. Except for points *6* and *14*, the position of each point in the series is altered by a 50° change in temperature. As previously described, silicates contain-

ing the β form of calcium orthosilicate show an anomalous viscosity. Omitting these—that is, points *8* and *20*—the effect of a rise of temperature from 1450° to 1500° C. is to interchange the positions of points *5* and *7*. This result is due to the increase in the temperature coefficient of viscosity that is noted in the mixtures of high alumina content. The arrangement of the quintuple points in the

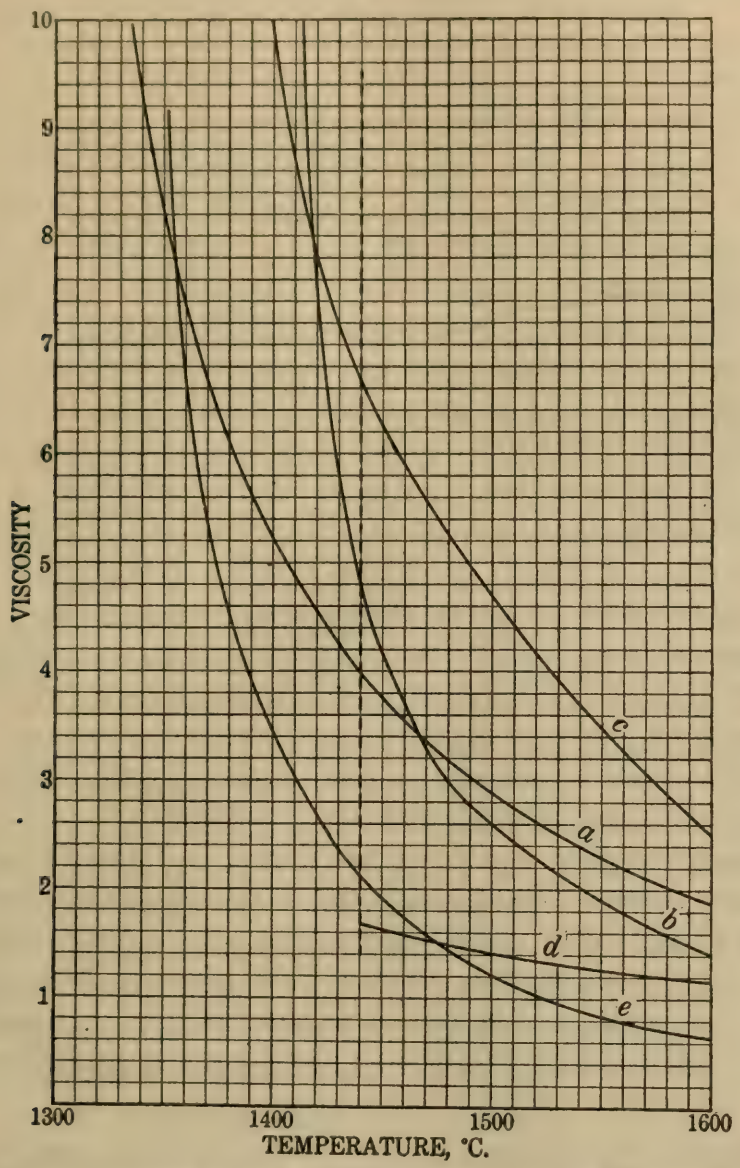

FIGURE 16.—Temperature-viscosity curves of binary eutectics. *a*, $CS\text{-}C_2AS$; *b*, $CAS_2\text{-}C_2AS$; *c*, $C_2S\text{-}C_2AS$; *d*, $C_3S_2\text{-}CS$; *e*, $CS\text{-}CAS_2$.

order of decreasing silica content is *2*, *5*, *6*, *7*, *14*, and in order of increasing alumina content, *6*, *2*, *5*, *7*, *14*. Obviously the viscosity for these points at the single temperature 1450° C. does not increase or decrease regularly with the content of silica or alumina. Arranged in order, however, of increasing lime content, the series is *2*, *7*, *5*, *6*, *14*, which agrees with the series for decreasing viscosity.

If the viscosities of the various binary eutectics shown in figure 16 be compared, the order of the curves in rank of decreasing viscosity at 1450° C. is *e*, *b*, *a*, *c*, *d*, where *e* refers to the binary eutectic metasilicate-anorthite, CS-CAS_2; *b* to CAS_2-C_2AS; *a* to CS-C_2AS; *c* to C_2S-C_2AS; and *d* to C_3S_2-CS.[a] The order of the eutectic compositions arranged in the order of decreasing silica content is *e*, *d*, *a*, *b*, *c*, and in the order of increasing alumina content is *d*, *a*, *c*, *c*, *b*. However, when arranged in the order of increasing lime content, they read *b*, *e*, *a*, *c*, *d*, which, except for the transposition of *e* and *b*, agrees with the order of decreasing viscosity. Figure 16 shows that this transposition is due to the high temperature coefficient of viscosity for the curve *b*, which represents the eutectic anorthite-gehlenite, containing 35 per cent Al_2O_3; below 1420° C. the curve *b* takes its proper position at the head of the viscosity series.

Hence, if any qualitative statement regarding the relation between viscosity and oxide composition can be made, it would seem that this must be confined to the general statement that the viscosity at analogous points in the various stability fields decreases with increasing lime content, and that the temperature coefficient of viscosity is greater for high alumina content. This is the limit of the conclusions that may be drawn from the present data; but it is possible that the same effect might be noted in comparing the viscosities of the various compounds, and possibly of similarly situated points on the binary systems. The general tendency toward lower viscosities for higher lime contents at analogous points is, however, much less in magnitude than the effects that are caused by the relative proportions of the compounds present in the liquid melt.

The conclusion that the melted silicate is a mixture not of oxides but of more complex compounds raises the question of whether the oxide can be correctly considered as the active constituent entering into the various reactions known to take place in these melts. For example, the reaction for the desulphurization of iron in contact with blast-furnace slag has usually been written as follows:

$$CaO+FeS+C \rightleftarrows CaS+Fe+CO.$$

Although it is permissible to assume that the lime compounds are subject to a certain amount of thermal dissociation, one should remember that evidence as to the degree of dissociation is entirely lacking. If one desires to write the hypothetical dissociation, say, of gehlenite, as

$$Ca_2Al_2SiO_7 \rightleftarrows CaSiO_3+CaAl_2O_4$$
$$CaSiO_3 \rightleftarrows CaO+SiO_2$$
$$CaAl_2O_4 \rightleftarrows CaO+Al_2O_3,$$

[a] Following the nomenclature of Rankin and Wright, C=CaO, A=Al_2O_3, and S=SiO_2.

it is certainly true that the final distribution of sulphur between the slag and the iron bath will depend upon the equilibrium constants in the four equations given. The conclusion is, therefore, that the desulphurizing power of a slag, as dependent on its composition, can not be expressed simply in terms of its percentage of CaO. For other important chemical reactions, such as the reduction of silica, a similar extension of the usual equation must be made.

In actual processes of practice, even an approach to equilibrium for such reactions is seldom attained. As is well-known, the time necessary for establishing equilibrium depends largely on the fluidity of the reacting liquid. It is certain, however, that the rigidity exhibited by silicate mixtures at low shearing stresses, which was never entirely absent in the mixtures examined, will have a decided effect on the reaction velocity. Seemingly no attention has been given to the kinetics of a heterogeneous reaction involving a "plastic fluid," and undoubtedly this factor would prove somewhat difficult to deal with theoretically. It might be reasonable to suppose that the driving force of certain reactions is less than the initial force required to overcome the rigidity of the liquid and produce the molecular displacement necessary for the progress of the reaction; then the liquid would act, in regard to such a reaction, essentially as a solid. In the somewhat similar process of diffusion of gold into lead, for example, the progress of molecular displacement, although exceedingly slow, has been noted; but as the knowledge of the mechanism of this process is slight, one can not say whether the great length of time required is due to the high viscosity, the high rigidity modulus, or the magnitude of the initial shear required to produce fluidity.

When an attempt is made to visualize the intimate nature of the processes taking place in the smelting of metallic ores, certain problems in the flow of viscous liquids have to be solved. This viscosity measurements described in this paper were made with the purpose of establishing the physical constants required in the consequent hydrodynamical equations. These constants are, of course, no less necessary to the study of the formation of igneous rocks. It is seen, however, that from the results obtained conclusions must be drawn that extend beyond the limits of these rather simple industrial and geological problems. They directly involve the little-studied chemistry of the silicates.

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